Chemical and X-ray analyses of five brands of dental gutta-percha cone

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Abstract

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Aim To determine the chemical composition of five commercially available nonstandardized gutta-percha points.

Methodology The organic fraction (gutta-percha polymer and wax/resin) of nonstandardized gutta-percha points (Dentsply^{TM}, Tanari^{TM}, Konne^{TM}, Obtura Spartan^{TM} and Analytic Endodontics^{TM}) was separated from the inorganic fraction (ZnO and $BaSO_4$) by dissolution in chloroform. Gutta-percha polymer was precipitated with acetone. Zinc oxide was partially separated from barium sulphate by reaction with HCl. Energy-dispersive X-ray microanalysis and X-ray diffraction were employed to identify the chemical elements and compounds (barium sulphate and zinc oxide). The barium sulphate content was calculated by percentage of sulphur from elemental microanalysis. All analyses were repeated three times.

Results The means and standard deviations of the percentage by weight of gutta-percha in the points were: Dentsply^{TM} (14.5 ± 0.70%), Tanari^{TM} (15.6 ± 0.66%), Obtura^{TM} (17.7 ± 0.35%), Konne^{TM} (18.9 ± 0.32%) and Analytic^{TM} (20.4 ± 0.40%). The mean and SD of the zinc oxide content were: Dentsply^{TM} (84.3 ± 0.50%), Tanari^{TM} (82.0 ± 0.72%), Obtura^{TM} (69.5 ± 0.21%), Konne^{TM} (78.0 ± 0.05%) and Analytic^{TM} (66.5 ± 0.50%).

Conclusions The method was appropriate to quantify gutta-percha and resin/wax components of gutta-percha points, but not barium sulphate and zinc oxide. An alternative procedure to determine barium sulphate and zinc oxide contents has been proposed based on elemental microanalysis of sulphur. Some brands of gutta-percha did not contain barium sulphate.

Keywords: composition, dental cone, gutta-percha.

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Introduction

Gutta-percha polymer is a *trans*-1,4-polyisoprene, obtained from the coagulation of latex produced by trees of the family Sapotaceae and is mainly derived from *Palaquium gutta* bail (Marciano *et al.* 1993). The *trans* isomer is more linear and crystallizes more easily than the *cis* isomer (natural rubber from *Hevea brasiliensis*). Thus, gutta-percha polymer is harder, more brittle, and less elastic than natural rubber (Spångberg 1998).

Gutta-percha is rigid at room temperature, becomes pliable at 25–30 °C, plasticizes at 60 °C, and melts (partial decomposition) at 100 °C (Budavari *et al.* 1996). The polymer becomes brittle and looses elasticity during storage and the degree of decomposition increases with storage time and temperature. As a result, it should be stored in a cool dry place for enhanced shelf-life (Spångberg 1998).

Modern gutta-percha cones are composed of organic (gutta-percha polymer and wax/resins) and inorganic components (zinc oxide, ZnO; barium sulphate, $BaSO_4$). Small percentages of colouring agents and antioxidants could also be present (Spångberg 1998). Substantial chemical heterogeneity is found amongst gutta-percha

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cones. Brittleness, stiffness, tensile strength, and radiopacity have been shown to depend primarily on the proportions of gutta-percha polymer and zinc oxide (Friedman *et al.* 1977). Antibacterial activity has been attributed to zinc oxide (Moorer & Genet 1982). Many commercial brands are available but only 15 of those have been analysed chemically (Friedman *et al.* 1977, Marciano & Michailesco 1989). In general, the composition has been shown to be approximately 18–22% gutta-percha polymer and 37–75% zinc oxide. The particular percentages of components vary according to the manufacturer. It is evident that since the cones differ in their composition, they may differ in their physical properties and even in their biological effect (Tagger & Gold 1988).

The objective of this study was to determine the chemical composition of five commercially available non-standardized gutta-percha cones. These cone brands were: Dentsply^{TM} (Petrópolis, Brazil), Tanari^{TM} (Macapuru, Brazil), Konne^{TM} (Belo Horizonte, Brazil), Obtura Spartan^{TM} (Jalisco, Mexico) and Analytic Endodontics^{TM} (Orange, USA).

Materials and methods

The gutta-percha cones studied are listed in Table 1. All samples were analysed before their expiring date.

In order to determine the chemical components of the cones, the procedure described by Friedman *et al.* (1977) (Fig. 1) was followed with modifications. To increase the mass of components obtained from the separation steps and so promote an increase in accuracy, 3 g of cones were used rather than 1.000 g. The dissolution of the inorganic material was carried out using 40 mL of 2.4 M HCl at 60°C for 15 min, in order to better promote the transformation (reaction) of zinc oxide, an insoluble compound, into zinc chloride ($ZnCl_2$), a soluble compound (chemical Equation A). After solvent and excess of acid evaporation, the solid was weighed. This mass (m_{ZnCl_2}) was transformed into zinc oxide mass (m_{ZnO}) using Equation 1. Barium sulphate was not attacked by the dilute acid at low temperature and remained as a solid material.

$$ZnO_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_2O \tag{A}$$

$$\begin{aligned} m_{ZnO} &= m_{ZnCl_2} \times \left(\frac{\text{molar mass of ZnO}}{\text{molar mass of ZnCl}_2}\right) \\ &= m_{ZnCl_2} \times 0.06 \end{aligned} \tag{1}$$

As gutta-percha has, in general, a slow dissolution process (Stevens 1999), the samples were placed in contact with 60 mL of chloroform for 24 h prior to the centrifugation. The gutta-percha polymer, insoluble in

Table 1 Dental gutta-percha cones size medium selected for study

Cone brand	Manufacturer/supplier	Lot number	Expiry date
Analytic^{TM}	Analytic Endodontics, Orange, CA, USA	110698	2001–11
Konne^{TM}	Konne Indústria e Comércio de Materiais Odontológicos, Belo Horizonte, MG, Brazil	–	2003–02
Obtura Spartan^{TM}	Precise Dental Internacional S.A., Jalisco, Mexico	9693 A	2003–01
Tanari^{TM}	Tanariman Ind. Ltda., Macapuru, AM, Brazil	011001G	2004–05
Dentsply^{TM}	Dentsply Indústria e Comércio Ltda., Petrópolis, RJ, Brazil	55448	2004–04

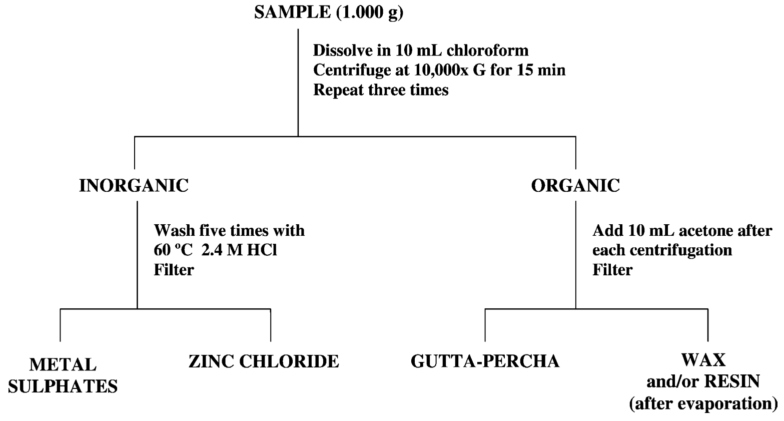

Figure 1 Scheme for separations of gutta-percha cone components suggested by Friedman *et al.* (1977).

acetone, was coagulated by addition of this solvent and weighed after total solvent evaporation. The mass of soluble material in acetone (wax/resin) was determined after solvent evaporation.

Energy-dispersive X-ray microanalysis was utilized to establish qualitatively the presence of chemical elements in the samples. The analysis was made in sections of all five brands mounted on aluminium stubs and carbon coated using a DSM-940 A scanning electron microscope (Carl Zeiss, Jena, Germany) with Link System 3.34 Series 300 with Si (Li) detector. The sections were analysed at ×1000 magnifications.

The apparatus used for the X-ray diffraction analysis was a Philips MDR Pro (Eindhoven, Holland) with 40 kV and 20 mA using a copper tube. The equipment was calibrated to give 100 cps. Each specimen was observed separately and compared with the X-ray diffraction pattern of zinc oxide and barium sulphate to verify the presence of these two compounds.

The quantitative determination of carbon, hydrogen, nitrogen and sulphur chemical elements in the samples was carried out in a microanalyser C, H, N, S/O Carlo Erba, Model 1110 (Rodano, Italy) with combustion at 1000 °C, in an oxygenated atmosphere. A thermal conductivity detector was employed. All the analyses were repeated thrice for all materials.

The organic fraction (gutta-percha polymer and wax/resin) was determined by the use of the procedure described by Friedman *et al.* (1977). Barium sulphate content was determined by sulphur percentage (elemental microanalysis) using Equation 2. Zinc oxide content was calculated by Equation 3, when the specimen contained sulphur, or by Equation 4, if not:

$$\begin{aligned}\mathrm{BaSO_4}\% &= \mathrm{S}\% \times \left(\frac{\text{molar mass of } \mathrm{BaSO_4}}{\text{atomic mass of S}}\right)\\ &= \mathrm{S}\% \times 7.28 \end{aligned} \qquad (2)$$

$$\begin{aligned}\mathrm{ZnO}\% = 100\% - (&\text{gutta-percha polymer}\%\\ &+ \text{wax/resin}\% + \mathrm{BaSO_4}\%)\end{aligned} \qquad (3)$$

$$\begin{aligned}\mathrm{ZnO}\% = 100\% - (&\text{gutta-percha polymer}\%\\ &+ \text{wax/resin}\%)\end{aligned} \qquad (4)$$

Results

The chemical composition of the five brands is shown in Table 2. Gutta-percha, wax/resin, metal sulphate, and zinc oxide were detected in all specimens. However, only the Obtura™ and Analytic™ specimens had barium and sulphur (Table 3). Zinc and oxygen were present as major elements in all brands. Barium sulphate and zinc oxide were identified in Analytic™ specimen (Fig. 2), as well as in Obtura™ brands but not in the other three brands (Konne™, Tanari™ and Dentsply™). The X-ray diffractogram (Fig. 3) associated with the Konne™ specimen is a representative example of the

Table 2 Chemical compositions of gutta-percha cones from different brands[a]

Cone Brand	Gutta-percha (mean% ± SD)	Wax/resin (mean% ± SD)	Metal sulphates (mean% ± SD)	Zinc chloride mass (g[b] mean ± SD)	Zinc oxide (mean% ± SD)
Analytic™	20.4 ± 0.55	2.0 ± 0.30	22.4 ± 0.22	2.76 ± 0.21	55.2 ± 4.28
Konne™	18.9 ± 0.32	3.1 ± 0.25	19.2 ± 4.21	2.94 ± 0.15	58.8 ± 3.16
Obtura™	17.7 ± 0.40	1.4 ± 0.20	23.5 ± 0.10	2.87 ± 0.02	57.4 ± 0.42
Tanari™	15.6 ± 0.64	2.4 ± 0.20	34.9 ± 2.12	2.35 ± 0.10	47.0 ± 2.00
Dentsply™	14.5 ± 0.70	1.2 ± 0.26	28.0 ± 3.21	2.82 ± 0.11	56.3 ± 2.18

[a] Based on method of Friedman *et al.* (1977).

[b] Mass obtained from 3 g of cone.

Table 3 Presence of minor and major components in five different brands of endodontic gutta-percha cones

Cone brand	Data from energy-dispersive X-ray microanalysis								
	Cl	Si	S	Ba	Fe	Ti	Ca	Zn	O
Analytic™		x	x	x		x	x	X	X
Konne™					x			X	X
Obtura™		x	x	x		x		X	X
Tanari™		x						X	X
Dentsply™	x	x						X	X

x, minor component; X, major component.

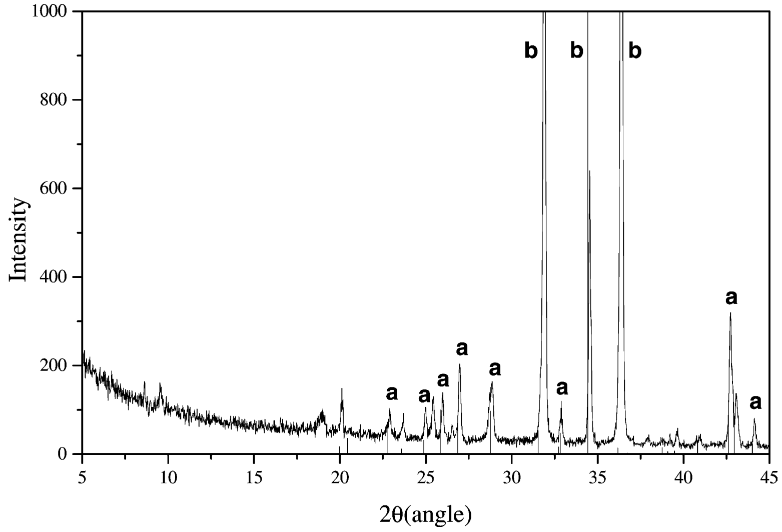

Figure 2 X-ray diffractogram of Analytic™ gutta-percha cone: (a) $BaSO_4$ pattern; (b) ZnO pattern.

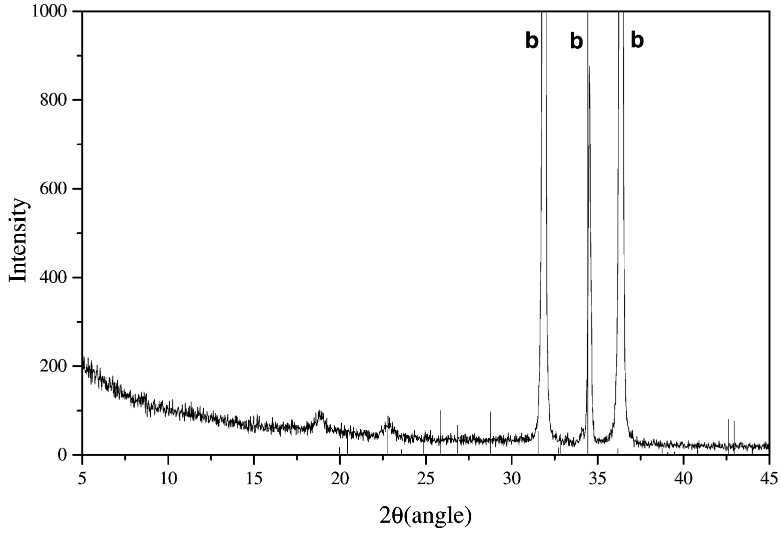

Figure 3 X-ray diffractogram of Konne™ gutta-percha cone: (a) $BaSO_4$ pattern; (b) ZnO pattern.

three brands without metal sulphate. The results indicate that the method of Friedman *et al.* (1977) was not accurate in quantifying inorganic components (ZnO and $BaSO_4$).

The chemical elements carbon, hydrogen and nitrogen were present in all five brands (Table 4); sulphur was present only in two specimens. The real composition of the five brands is shown in Table 5. The amount of

Table 4 Elemental microanalysis of cones from different brands

Cone brand	Percentage of chemical elements (mean ± SD)			
	Carbon	Hydrogen	Nitrogen	Sulphur
Analytic™	20.76 ± 0.09	2.97 ± 0.04	0.26 ± 0.12	1.52 ± 0.05
Konne™	19.49 ± 0.25	2.85 ± 0.06	0.45 ± 0.04	0
Obtura™	17.49 ± 0.15	2.57 ± 0.06	0.17 ± 0.02	1.56 ± 0.16
Tanari™	16.59 ± 0.07	2.45 ± 0.01	0.36 ± 0.03	0
Dentsply™	16.15 ± 0.03	2.47 ± 0.08	0.29 ± 0.29	0

Table 5 Real compositions of gutta-percha endodontic filling materials

Cone brand	Gutta-percha	Wax/resin	Metal sulphates	Zinc oxide
Analytic™	20.4 ± 0.40	2.0 ± 0.15	11.1 ± 0.22	66.5 ± 0.50
Konne™	18.9 ± 0.32	3.1 ± 0.32	Not present	78.0 ± 0.056
Obtura™	17.7 ± 0.35	1.4 ± 0.20	11.4 ± 0.07	9.5 ± 0.21
Tanari™	15.6 ± 0.66	2.4 ± 0.20	Not present	82.0 ± 0.72
Dentsply™	14.5 ± 0.70	1.2 ± 0.24	Not present	84.3 ± 0.50

All values are expressed in mean% ± SD.

Table 6 Comparison between ranges of components percentage of gutta-percha cones obtained from different authors and brands

Gutta-percha polymer (%)	Wax/resin (%)	Organic fraction (%)	Barium sulphate (%)	Zinc oxide (%)	Inorganic fraction (%)	Reference
18.9–21.8	1.0–4.1	22.7–23.8	1.1–17.3	59.1–75.3	75.3–76.9	Friedman *et al.* (1977)[a]
		17.7–45.7	3.2–31.2	36.6–74.6	54.3–82.3	Marciano & Michailesco (1989)[b]
14.5–20.4	1.2–3.1	15.7–22.4	0–11.4	66.5–84.3	77.6–84.3	This work

[a] Five commercial brands were studied (Premier, Mynol, Indian Head, Dent-O-Lux, Temprite).

[b] Ten commercial brands were studied (Hygienic, Mynol, Roeko, Detrey, Becht, Septodont, Medico-Dentaire, IFKER, SPAD, Endoset).

gutta-percha polymer ranged from 14.5 to 20.4% and zinc oxide from 66.5 to 84.3%.

In Table 6, the data obtained from the present study are compared with results of Friedman *et al.* (1977) and Marciano & Michailesco (1989).

Discussion

The barium sulphate content when determined by the method of Friedman *et al.* (1977) is overestimated (Table 2). This probably occurs because washing at 60 °C with 2.4 M HCl was not sufficient to promote the separation of all the zinc oxide from the barium sulphate. In fact, the insoluble residue after reaction with HCl, observed in those brands that did not contain barium sulphate, is wrongly assumed to be barium sulphate.

Increasing the reaction time up to 150 min, the reaction temperature up to 95 °C, the wash repetition to 5, and HCl concentration to 6.0 M were attempted. As the method of Friedman *et al.* (1977) did not give a reliable quantification of inorganic components another procedure was developed.

The X-ray microanalysis (Table 3) provided an overview of the chemical elements of gutta-percha cones. Zinc and oxygen are present in large amounts, reflecting the fact that zinc oxide is the main component (Möller & Ørstavik 1984).

The occasional occurrence of small amounts of Cl, Ti, Ca and Si is most probably due to impurities or small volumes of compounds added during manufacturing. Ti, Ca and Si may be present as oxides, like TiO_2, CaO and SiO_2, and Cl as $ZnCl_2$.

The presence and absence of zinc oxide and barium sulphate was unequivocally determined by X-ray diffraction. This technique corroborates the X-ray microanalysis results, which indicate the presence of zinc oxide in all five brands and absence of barium sulphate in three of them (Konne™, Dentsply™, Tanari™).

Despite the relevance and importance of the X-ray microanalysis and diffraction techniques in the screening of some chemical elements and compounds present in gutta-percha cones, there are some limitations in the use of these techniques for quantitative analysis. For rigorous quantitative X-ray microanalysis, the atomic number of the analysed element has to be greater than 11. Thus, important elements like hydrogen, carbon, nitrogen and oxygen could not be correctly quantified. In addition, the element concentration has to be greater than 5% and the specimen has to be homogeneous in the volume sampled (Lyman *et al.* 1990). The X-ray diffraction (powder diffraction) is very useful to identify crystalline substances, such as the inorganic compounds $BaSO_4$ and ZnO, but it is not normally used to quantify them.

The most popular technique to quantify C, H, N and S is elemental microanalysis. The results demonstrated that carbon percentage is proportional to gutta-percha polymer content (Table 4). The presence of nitrogen could be due to antioxidants added to the cones or to protein aggregated to natural gutta-percha polymer, very common in natural rubbers from different origins (Hasma & Othman 1990, Rodrigues *et al.* 1998).

The gutta-percha polymer and zinc oxide contents were at lower and higher ranges, respectively, than those determined by Friedman *et al.* (1977) (Table 6). Wax/resin content was in the same range. The most significant difference was in barium sulphate percentage. Friedman *et al.* (1977) detected the presence of $BaSO_4$ in all cone brands studied. In three of the five brand formulations analysed, barium sulphate was not detected. Barium sulphate and zinc oxide provide radiopacity (Spångberg 1998). As barium is a chemical element with larger atomic number than zinc, $BaSO_4$ absorbs X-rays more readily than ZnO. It means that the absence of barium sulphate will decrease gutta-percha radiopacity. The influences of barium compound in physical and clinical properties of cones have not been determined.

The chemical compositions of gutta-percha points vary according to the manufacturer specially in the proportions of gutta-percha and zinc oxide. This may lead to variations in brittleness, stiffness, tensile strength, and radiopacity (Friedman *et al.* 1977, Gutmann & Witherspoon 1998) and also in flow, plasticity, elongation, inherent tension force, and thermal behaviour (Friedman *et al.* 1977, Tagger & Gold 1988, Marciano & Michailesco 1989, Marciano *et al.* 1992).

Conclusion

Within the limits of this study the following conclusion could be obtained:

1 The method described by Friedman *et al.* (1977) was appropriate to quantify gutta-percha and resin/wax components of cones, but led to overestimation of barium sulphate and underestimation of zinc oxide content.

2 An alternative procedure to quantify barium sulphate and zinc oxide has been proposed based on elemental microanalysis of sulphur.

3 The gutta-percha and zinc oxide contents ranged 14.5–20.4 and 66.5–84.3%, respectively.

4 Cone brands without barium sulphate were found.

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